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APPENDIX A

Retrieval and Molecular Sensitivity Studies for the Global Ozone Monitoring
Experiment and the SCanning Imaging Absorption spectroMeter for Atmospheric
CHartography

Retrieval and Molecule Sensitivity Studies for the Global Ozone Monitoring Experiment and the
SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY

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ABSTRACT

The Global Ozone Monitoring Experiment (GOME) and the SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) are diode array-based spectrometers that will make atmospheric constituent and aerosol measurements from European satellite platforms beginning in the mid 1990's. GOME measures the atmosphere in the UV and visible in nadir scanning, while SCIAMACHY performs a combination of nadir, limb, and occultation measurements in the UV, visible and infrared. We present a summary of the sensitivity studies that have been performed for SCIAMACHY measurements. As the GOME measurement capability is a subset of the SCIAMACHY measurement capability, the nadir, UV and visible portion of the studies shown here apply to GOME as well.

1. INTRODUCTION

SCIAMACHY sensitivity studies include its three measurement geometries: nadir observing, viewing the earth's limb in scattered light, and solar and lunar occultations. In nadir observation alone, profile information is determinable in some cases by differential penetration of backscattered light at different wavelengths (as in TOMS/SBUV), and by the variable temperature structure of some molecular absorptions. Height resolution from nadir measurements is limited to 8-10 km from differential penetration and 3 km in favorable cases using temperature structure. Height resolution in limb viewing is 3 km, limited by the weighting functions for limb scattering and by the spacecraft stability. Height resolution is also 3 km for occultations, limited primarily by the telemetry data rate; 1 km resolution would otherwise be possible. The quantities retrieved from SCIAMACHY measurements include:

Nadir observations: Total column amounts of O₃, O₄, O₂, CO, H₂O, CH₄, CO₂, NO₂, N₂O, HCHO, SO₂, ClO, OClO, and BrO; stratospheric profiles of O₃, CO, H₂O, CH₄, CO₂, N₂O; the column of NO above the ozone layer; tropospheric profiles or columns of O₃, CO, H₂O, CH₄, CO₂, N₂O. Stratospheric profile information, discrimination between stratospheric and tropospheric columns, and, in some cases, tropospheric profile information is derived from the temperature dependences of the absorption features.

Limb viewing observations: Stratospheric profiles of O₃ (20-50 km), O₂(¹Δ) (50 km-90 km), O₂ (20-50+ km), CO (20-35 km), H₂O (20-53 km), CH₄ (20-40 km), CO₂ (20-50+ km), NO (40-140 km), NO₂ (20-40 km), N₂O (20-35 km), BrO (20-25 km under normal conditions; 20-30 km under ozone hole conditions).

Solar/lunar occultations: Stratospheric profiles of O₃ (15-50 km), O₂ (15-50+ km), CO (15-35 km), H₂O (15-53 km), CH₄ (15-40+ km), CO₂ (15-50+ km), NO₂ (15-40 km), N₂O (15-35 km), BrO (15-35 km under normal concentrations). Occultations are more infrequent than limb scattering observations, and are limited to latitudes of 50-80°, but provide the most sensitive and precise profile retrievals.

Tropospheric amounts from limb-nadir subtraction: Tropospheric columns of O₃, CO, H₂O, CH₄, CO₂, NO₂, N₂O.

Clouds and aerosols: SCIAMACHY will obtain aerosol data in occultation, limb-scattering and nadir measurements. Stratospheric aerosol measurements include background aerosol, Junge layer, and polar stratospheric clouds (PSCs); tropospheric aerosols, including clouds, sand winds, and soot from forest fires.

2. MOLECULE SENSITIVITY STUDIES

The sensitivities for retrievals of molecular species concentrations as functions of altitude have been extensively studied, under a wide variety of geographic conditions, in order to accurately gauge the capabilities of the SCIAMACHY instrument. Calculations are performed for all of the SCIAMACHY modes of measurement, including nadir viewing, viewing of the earth's limb in scattered light, and solar and lunar occultations. Note that simultaneous nadir and limb measurements are the normal mode of operation for the majority of dayside portion of each orbit. The calculations include realistic expectations of detector quantum efficiency and noise performance, and the instrument etendue and optical throughput that are derived from the Phase A instrument study.

Retrieval studies for atmospheric molecules are performed using atmospheric concentration profiles from the MPI Mainz global 1-D and 2-D models (C. Brühl, R. Hennig and P. Crutzen, private communication), calculated with clean and polluted air, daytime, conditions. Additional information on nighttime NO₃ comes from Norton and Noxon, 1986.¹ Constant mixing ratios are assumed for CO₂ (340 ppm) and O₂ (20.95%). The simulations assume exposure times of 2 seconds in nadir spectra, 1.5 second in limb spectra and lunar occultations (appropriate to 3 km vertical resolution), and short exposure times in solar occultation, with the constraint that exposures are limited to 10⁸ photons/pixel in the most highly illuminated portion of each detector array. Interferences from other absorbing species are included in the studies for each individual molecule. Current studies are limited to a maximum pressure altitude of 60 km because of the limitation of the model calculations to the stratosphere. In practice, profiles for at least O₂, O₃, and CO₂ will extend to higher altitudes.

Spectra for the simulations are taken from the best available sources, including digitally acquired electronic spectra obtained in the laboratory at MPI Mainz. Spectra in the infrared portion are simulated using the 1986 HITRAN line parameter listing.²

Calculations of geometries are performed with multilayer, curved-shell models, including refraction, to provide line of sight column densities as functions of temperature, pressure, and altitude. Calculations in the UV and visible parts of the spectrum are made using the AFGL LOWTRAN7 code, including multiple scattering in the nadir and limb geometries. Calculations in the infrared are performed with LOWTRAN7 and with the Smithsonian Astrophysical Observatory line-by-line radiance code.³ Most calculations are made with the earth's average albedo of 0.3. The effect of surface spectral reflectance on nadir measurements was investigated in more detail, as discussed further below. Lunar occultations are considered for the measurement of NO₃, as discussed in the section for that molecule.

The 2-D model results used in the calculations are for January 1, with global coverage extending from 85°S to 85°N, which samples a very representative set of the earth's atmospheric conditions. Most calculations are done at 35°N, which corresponds to a solar zenith angle of 63.4° for the EPOP 10:00 crossing time. The effect of other solar zenith angles on measurements in the nadir and limb geometries, including measurements in polar regions, was investigated in some detail, as discussed below.

The solar illumination used in these studies is the LOWTRAN7 solar source function. Aerosol and molecular scattering are also from LOWTRAN7. 20 km is taken as a practical lower limit for limb scattering measurements due to confusion by multiple scattering at lower tangent heights. 15 km is taken as the lower limit for occultation measurements because of atmospheric refraction and extinction by aerosols. It is hoped that, in practice, both of these limits can be extended downward. The anticipated EPOP spacecraft jitter of 0.01° corresponds to 0.57 km at the limb, or 8% in airmass. We combine this with the effect of multiple scattering on limb retrievals: Mount *et al.*, measured NO₂ in limb scattering with "negligible" effects due to multiple scattering down to 28 km, with the Solar Mesosphere Explorer satellite, using wavelengths from 430 to 450 nm.⁴ SCIAMACHY obtains significant information on NO₂ and O₃ out to 500 nm implying, for Rayleigh scattering varying as $1/\lambda^4$, negligible confusion due to multiple scattering down to 25 km. Thus, we estimate limb measurement errors in precision for profile determinations, discussed further below for individual molecules, of 10% above 25 km and 20% from 20-25 km, unless further limited by the signal to noise ratios of the measurements for such molecules. Determination of stratospheric columns from limb measurements in this wavelength range, particularly for species with concentrations which peak in the stratosphere, will be somewhat more precise, since the multiple scattering predominantly causes smearing of profile information over a scale height about the tangent altitude. Species measurements in the stratosphere using limb scattering at significantly shorter wavelengths will provide only limited profile information due to the larger effects of multiple scattering. Limb measurements at longer wavelengths, particularly in the infrared, are less affected by multiple scattering. Nadir and solar occultation measurement capabilities are calculated using a lower limit of 1% for measurement precision due to the difficulty of making more precise measurements and calibrations. We hope, of course, to be able to achieve higher precision in practice so that this technique will be capable of determining long-term trends in global O₃.

Sensitivity and interference studies for some species to be measured in the infrared are checked by examining a high resolution (0.007 cm⁻¹) solar spectrum from Kitt Peak National Observatory (KPNO), obtained courtesy of D. W. Johnson and G. Stokes. The spectrum was taken as part of the BIC campaign, under clean tropospheric conditions, at 1.1 airmass. Confirmation of O₄ is from a 1.0 airmass high resolution visible solar spectrum from KPNO (courtesy of R. Kurucz).

Figure 1 shows the solar spectrum as measured by SCIAMACHY, including the etendue, optical throughput, detector quantum efficiency (normalized to photons pixel⁻¹ s⁻¹ for the various detector channels), and the beam dilution (18% of the instrument field of view is filled by the sun when SCIAMACHY views the central part of the solar disk).

A molecule by molecule discussion of the retrieval studies follows. The results are summarized in Figure 2, which shows altitude ranges for profile retrievals, and Table 1. The altitude limits shown here are for retrieval to a 3 km vertical resolution with $\leq 10\%$ uncertainty in the concentrations, excluding uncertainties in cross-sections, for the stratosphere, plus the altitudes over which any tropospheric information can be obtained. These limits are derived from the January 1, 35°N studies, implying a solar zenith angle of 63.4°, as mentioned previously. For most molecules they are valid for solar zenith angles of up to at least 80°. Molecules which may possibly be measured by SCIAMACHY but are not included in the the studies due to the lack of suitable available laboratory spectra include O(³P), HO₂, and HONO.

2.1 Molecules in the normal atmosphere

O₃ concentrations are retrieved from SCIAMACHY measurements using the ultraviolet (Hartley and

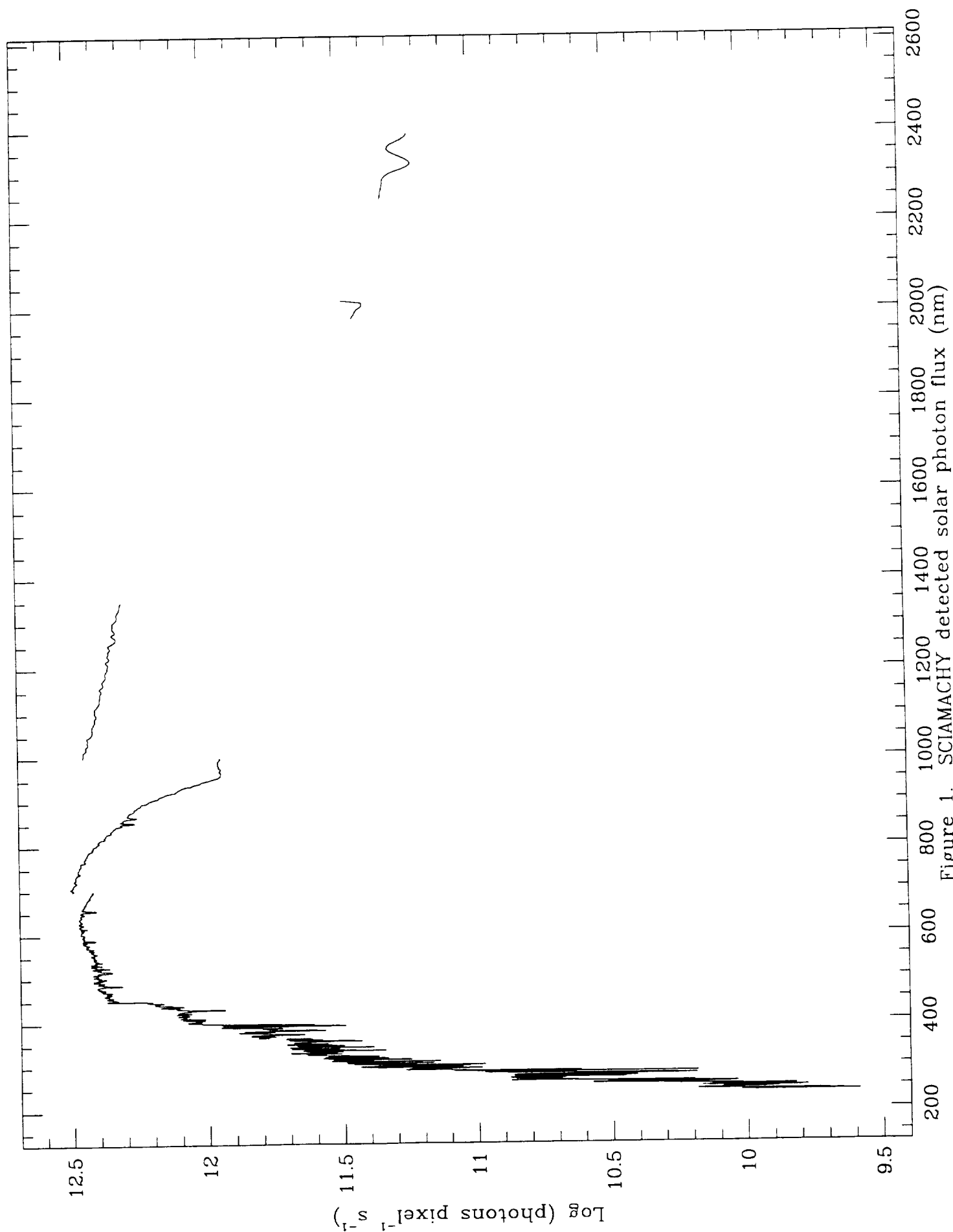
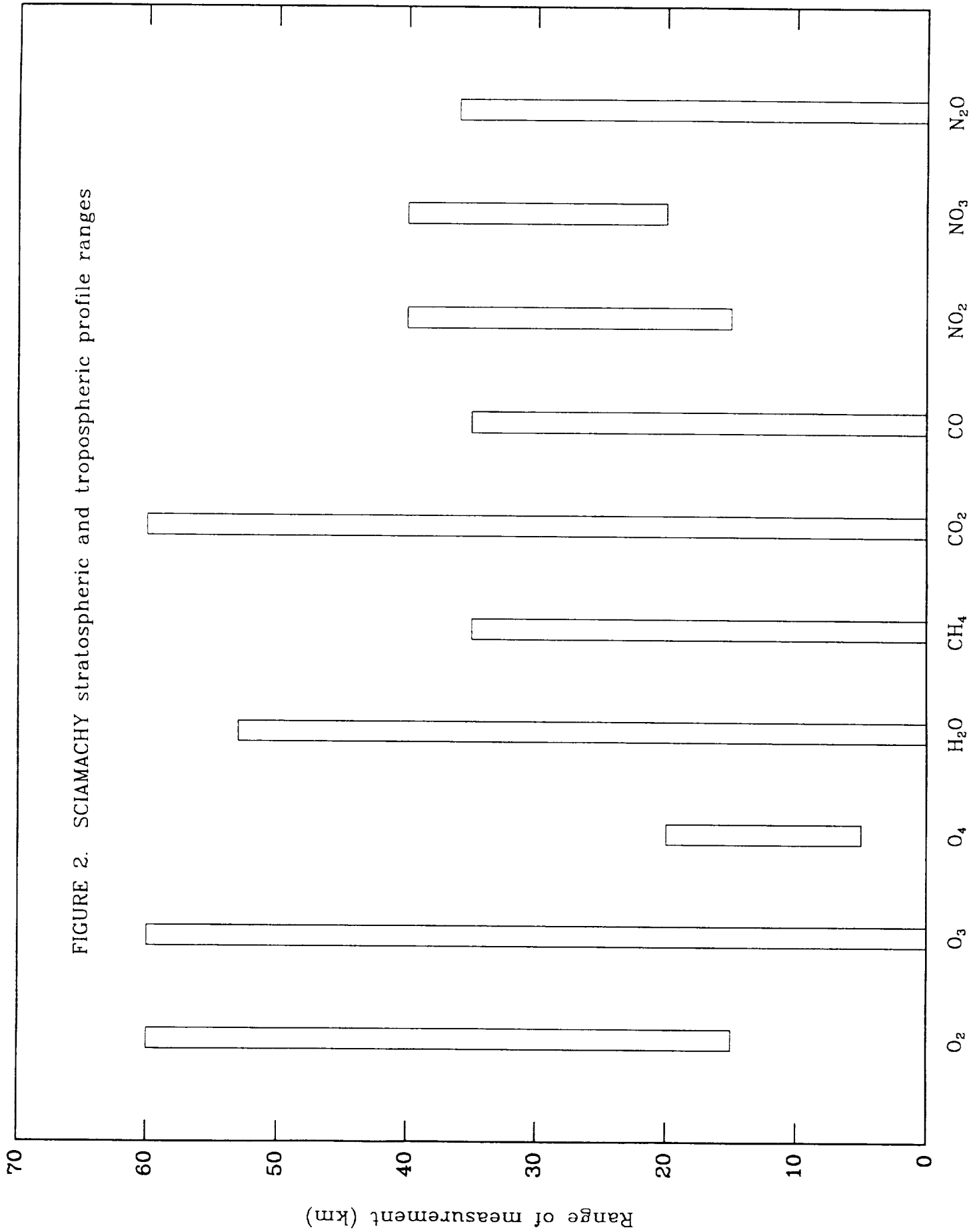


Figure 1. SCIAMACHY detected solar photon flux (nm)

FIGURE 2. SCIAMACHY stratospheric and tropospheric profile ranges



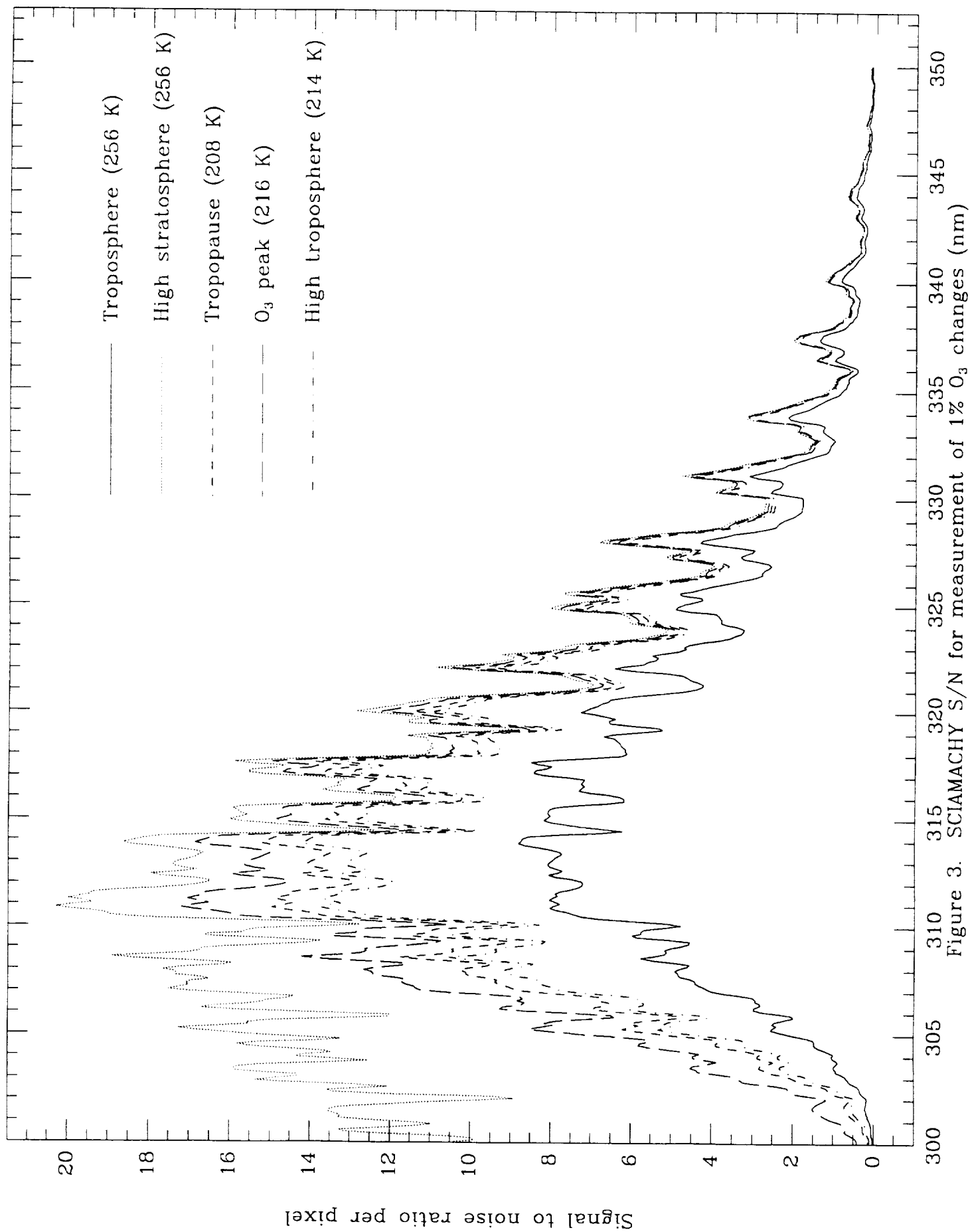
Huggins) bands and the visible (Chappuis) bands. Precise determinations of column O_3 are obtainable from Chappuis band measurements. Measurements of the UV bands, using knowledge of penetration depth as a function of wavelength to obtain stratospheric profile information, has become a standard technique for satellite ozone measurements. This differential penetration is measured using a number of discrete wavelength channels that are much broader than the SCIAMACHY resolution elements. Thus, SCIAMACHY includes this type of measurement as a subset of its O_3 measurements.

SCIAMACHY can also measure ozone profiles in the limb scattering geometry, up to at least 50 km in most geographic locations. Although the signal to noise ratio in these measurements is quite high, the precision of concentration profiles from limb measurements will be limited to ca. 10% above 25 km and 20% from 20-25 km due to the mixing of light from various sources in the multiple scattering process. Stratospheric column O_3 from limb measurements can be determined to 10% since limb measurements extend down to at least 1/2 scale height below the O_3 peak.

A strength of the SCIAMACHY instrument is that it can provide extensive maps of tropospheric ozone. Some determinations of tropospheric O_3 in tropical regions have been made in recent studies by subtracting stratospheric O_3 , measured by the SAGE instrument, from TOMS total ozone measurements.⁵ SCIAMACHY includes the UV bands used in past and present satellite instruments for measuring O_3 , but affords continuous coverage of the region above 240 nm, and at significantly higher resolution. This allows us tremendous leverage in retrieval of tropospheric ozone profiles due to the temperature dependent structure of the Huggins bands.^{6,7} The Huggins bands have discrete vibrational structure between 300 and 370 nm, with features having widths significantly less than 1 nm. This is the sharpest vibrational structure of any electronic band of O_3 that has been studied. This structure has strong temperature dependence due to the onset of thermal population of excited vibrational levels in the electronic ground state. It is this temperature dependent structure that provides a spectral signature for tropospheric ozone; its differential character derives from the onset of weaker band absorption between the stronger absorption peaks, which are due to absorption from O_3 (000). One may think of the differential of the O_3 spectrum with temperature as part of a basis set used to match the observed spectrum. Note that tropospheric ozone is significantly warmer than stratospheric ozone at any altitude in the stratosphere where there is significant O_3 . Thus, the tropospheric O_3 column is simply obtainable from an instrument with the resolution and sensitivity of SCIAMACHY. Determination of the complete altitude profile, including the troposphere, requires the development of a more sophisticated algorithm, which will include differential penetration and the Chappuis band column measurements. Figure 3 shows the sensitivity of the nadir spectrum as measured by SCIAMACHY, at the SCIAMACHY resolution, for 1% changes in total ozone column at various levels in the atmosphere. The sensitivity is shown as signal to noise ratio per pixel that can be achieved in 2 seconds of averaging time by SCIAMACHY in measuring these 1% differences at different altitudes. Figure 3 was performed using the full multiple scattering formalism of LOWTRAN7, to show the larger characteristics of the radiance changes due to ozone distribution. This does not, however, fully model the temperature dependence of the bands. Our sensitivity studies indicate that SCIAMACHY can achieve a precision corresponding to at least 1% of the total column ozone for retrieval of O_3 to 3 km vertical resolution throughout the stratosphere and troposphere.

We have calculated the ability of SCIAMACHY to measure polar ozone depletion. Calculations are performed using a solar zenith angle of 80° , appropriate to 80° N-S at the equinox. Moderate ozone hole conditions are simulated by removing 20% of the total column ozone from atmospheric above the tropopause, symmetric about the ozone peak. The nadir measurements will be able to measure polar ozone depletion to the full geographic coverage of the orbit. SCIAMACHY should also be able measure polar ozone depletion in the limb geometry to even higher latitudes, down to quite low solar zenith angles. The geographic limits to high latitude for this type of measurement are difficult to estimate precisely at present due to the difficulty in estimating the light levels under these conditions.

As an additional check on the ability of SCIAMACHY to retrieve stratospheric ozone profiles, and to distinguish between stratospheric and tropospheric ozone, we have calculated the ability of SCIAMACHY



to measure stratospheric O_3 in solar occultation, chiefly using the Chappuis bands, so that the tropospheric residual may be obtained by subtraction. The signal to noise ratio per pixel for measurements of the Chappuis bands at their peak for these measurements, which correspond to a vertical resolution limited only by the slit size (1 km), is tremendous, and there are a large number of pixels covering the Chappuis bands. The implied measurement precisions are extremely high, and will be limited in practice by other factors, such as spacecraft pointing and intensity calibration. SCIAMACHY will be able to measure O_3 to better than 1% precision for each 3 km height interval from 20-40 km, assuming solar tracking to sufficient precision, and to better than 5% for the total stratospheric column. This is sufficient precision to quantitatively test the determination of tropospheric O_3 from the temperature dependence of the Huggins bands under conditions of relatively high tropospheric O_3 , and to provide for some independent mapping of tropospheric O_3 at modest precision and geographic coverage. Stratospheric measurements in solar occultation extend at lower precision to at least the stratopause.

In summary, SCIAMACHY can determine the ozone column density quite accurately from the nadir measurements (to better than 1% precision); it can determine profiles to better than SBUV precision from the nadir measurements; it can cleanly distinguish between tropospheric O_3 and stratospheric O_3 from the nadir measurements and give moderate (1% of total column ozone) profile information in the troposphere; it can provide further stratospheric profile information at moderate precision from the limb scattered light; it can provide stratospheric profile information (and possibly upper tropospheric profile information) with very limited geographic coverage from solar occultation measurements, with sufficient precision to test the algorithm for determination of tropospheric O_3 from nadir measurements; it can make precise measurements of polar ozone depletion to at least 80° latitude, and probably further. The SCIAMACHY measurements of ozone are not subject to long-term degradation of the type suffered by SBUV/TOMS, as discussed in the instrumentation section of this report.

$O_2(^1\Delta)$. Quantitative laboratory spectra of $O_2(^1\Delta)$ are not available for a sensitivity limit study, but the positions are well known. Absorption by tropospheric ground state oxygen to the $^1\Delta$ state is quite prominent in the infrared spectrum. This absorption masks the emission by $O_2(^1\Delta)$ in the nadir observations. $O_2(^1\Delta)$ is used by the Solar Mesosphere Explorer satellite in limb scattering observations to determine the O_3 profile from 50-90 km;⁸ SCIAMACHY will be able to measure it in limb scattering for the same purpose.

O_4 . Quantitative laboratory O_4 spectra are not available for a sensitivity study. As it is quite prominent in the solar spectrum observed from the ground. As it is a van der Waals molecule, and thus has a concentration strongly dependent upon temperature and pressure, it is a useful diagnostic for cloud top and boundary layer height.

O_2 concentrations provide a cross-check of the pointing calibration in occultation and limb measurements. In the nadir view, penetration depth determinations from O_2 provide information about cloud and boundary layers heights. O_2 absorbs very strongly in the atmosphere, chiefly near 690 and 760 nm. O_2 column measurements will have a precision of 1%, our projected limit for strong absorbers. O_2 measurements in the limb and occultation geometries will also have the limiting sensitivity up to at least the stratopause.

CO. The $2 \leftarrow 0$ vibrational overtone band of CO lies between 2.3 and 2.4 μm . SCIAMACHY can be used in nadir view to measure the CO column abundance with a sensitivity limit of $2 \times 10^{16} \text{ cm}^{-2}$, corresponding to 1% of background tropospheric CO, when the earth's reflectance at these wavelengths is as low as 0.1. The simulations have taken proper account of solar CO, which has lines of comparable size to the absorption from background terrestrial CO at about $m = 9$ and higher, but which is divided out by our solar calibrations and which, in any case, has very characteristic spectrum differences due to the much higher temperatures of solar CO. Since the tropospheric CO measurements are fundamental to the success of SCIAMACHY, the results of the simulation are checked by examining the KPNO infrared solar spectrum. The CO lines are quite prominent in the spectrum, as predicted, with most lines being sufficiently separated

from interfering H_2O and CH_4 to be cleanly measurable at the SCIAMACHY resolution. Additionally, we have calculated the ability of SCIAMACHY to measure CO in the limb geometry, by comparing the limb-scattered radiation strength with the MPI model CO concentration values and the CO line strengths. Stratospheric CO absorption can be measured with a precision ranging from 1.5% at 20 km to 15% at 30 km (by 35 km the precision has dropped to 50%). In practice, due to effects of multiple scattering, the determination of total stratospheric CO will be precise to 10-15%. Since only ca. 5% of the column CO is expected to be in the stratosphere, the limb measurements will provide for a correction to the column tropospheric CO to better than 1%. Limited CO profile information for the troposphere will be available from the differential temperature dependence of the various CO lines in nadir observing. CO is also measurable at very high signal to noise ratios in solar occultation spectra. ^{13}CO has line strengths down by a factor of 0.011 from ^{12}CO , due to the ^{13}C isotopic abundance. It will be readily measurable in the lower stratosphere in solar occultation. There is a marginal possibility that the column of ^{13}CO will be measurable from signal averaging of nadir spectra.

H_2O absorbs strongly between 700 and 1000 nm, and in the vibrational overtone bands near 2400 nm. The strong temperature dependence of these latter bands allows retrieval of the altitude profile of tropospheric H_2O in the nadir view. H_2O is retrievable in all SCIAMACHY measurement geometries to the limits of the SCIAMACHY technique - 1% in nadir, 10-20% in stratospheric profile from limb measurements, 1% in stratospheric profile from solar occultation, and 10% per 3 km interval in tropospheric profile from deconvolution of the temperature-dependent nadir spectrum.

CH_4 has strong vibration overtone absorption from 2200 to 2400 nm. As with H_2O , the temperature dependence allows retrieval of the tropospheric altitude profile from the nadir view. The limits for CH_4 profile measurements in limb-scattered light extend to 40 km in the stratosphere, due to the high concentration of CH_4 and the strength of the absorption. The column amount of $^{13}\text{CH}_4$ will almost certainly be measurable with SCIAMACHY to good precision, since 1.1% of $^{12}\text{CH}_4$ is readily measurable. However, line positions and strengths for $^{13}\text{CH}_4$ are not currently catalogued, so it is not possible to further quantify its measurement.

CO_2 has its strongest overtone absorption between 1900 and 2200 nm. As with H_2O and CH_4 , the temperature dependence can be used to retrieve the tropospheric profile in the nadir view. The CO_2 absorption is so strong that the retrieval of CO_2 in all geometries is limited only by the SCIAMACHY baseline precision considerations. We note here that the SCIAMACHY CO_2 measurements are fully as capable of providing atmospheric pressure and temperature information as the standard 15 μm infrared technique, since the band used (the strongest overtone absorption of CO_2) originates from the ground state and thus supplies the same information about the distribution in energy levels of atmospheric CO_2 . It may be possible to use this CO_2 information to partly correct for the effects of spacecraft jitter on limb measurements, but such corrections have not been included in the present calculations.

NO. The NO profile above the ozone layer (from 40-140 km) can be determined from SCIAMACHY limb and occultation measurements using the (1,4), (1,6), and (0,3) gamma bands which fluoresce from 255-280 nm, as determined in model sensitivity studies by Frederick and Abrams.⁹ In nadir view, gamma band emission gives a column amount for NO above where O_3 absorbs strongly.

NO_2 concentrations are retrieved from the uv-visible absorption between 300 and 600 nm. In limb viewing NO_2 is readily observed in the stratosphere as already shown by SME, and by balloon measurements using this technique.¹⁰ Stratospheric NO_2 is measurable to 10% precision from 25-40 km and 20% precision from 20-25 km in limb viewing, limited by the considerations discussed earlier. Stratospheric column determinations from limb viewing are good to 10%. In occultation, the profile will be measurable to 1% precision from 40 to below 20 km. In nadir viewing the total column is observed to the limiting 1% precision. From these two measurements tropospheric NO_2 amounts may be determined under some conditions. SME

measured NO_2 column amounts above 28 km in the range $1\text{--}3 \times 10^{15}$ molecule cm^{-2} .^{4,11} This corresponds closely to the total NO_2 column abundances measured by SAGE.¹² A background tropospheric mixing ratio of 30 pptv yields a tropospheric column amount which is approximately an order of magnitude lower. In background clean air conditions deconvoluting the stratospheric and tropospheric amounts from SCIAMACHY data is marginal. In polluted air this task becomes much simpler. For 3×10^{15} cm^{-2} stratospheric NO_2 , the column uncertainty is 3×10^{14} cm^{-2} , which corresponds to a tropospheric limiting concentration of 16 pptv for $S/N = 1$. Tropospheric NO_2 in even moderately polluted regions is substantially larger than this. In such regions, the limit for tropospheric column becomes the 1% precision of the total column NO_2 . The tropospheric column can be determined to at least 10% precision for concentrations above 160 pptv. The NO_2 absorption features are known to be temperature dependent, which in nadir view may assist further in the differentiation of tropospheric and stratospheric amounts.

NO_3 . The nighttime concentration of NO_3 has been measured successfully by absorption of lunar and stellar light.¹³ The strongest NO_3 absorption, between 660 and 665 nm, is 2–3% deep in the occultation geometry for tangent heights of 28–38 km. Using lunar occultation we will be able to measure the profile of NO_3 , when the lunar cycle permits, with potential long-term latitude coverage of 50–80° N and S.¹⁴ The scan system can observe in both hemispheres, but the spacecraft accommodation will probably imply that the moon will only be observable in one hemisphere. Studies will be made in Phase B of the possible use of planets and stars (e.g., Venus) for nighttime occultation measurements. This is a significant portion of the region where enhanced NO_3 is expected in polar night conditions. The lunar occultation signal measured by SCIAMACHY is down from the solar occultation signal by a factor of 1.2×10^{-6} due to the geometric factors and the lunar albedo. For NO_3 at 30 km, using 1.5 second integration time, the numbers of photons per pixel at 660–665 nm is 4.2×10^6 for a signal to noise ratio per pixel of 2.0×10^3 . For 2% absorption at band center, the NO_3 is measured with 2.4% precision.

N_2O . The $00^0_2 \leftarrow 00^0_0$ vibrational overtone band of N_2O lies between 2.25 and 2.30 μm . Lines of N_2O are quite prominent in the Kitt Peak solar spectra, with many individual lines well separated from interferences at the SCIAMACHY level. The N_2O column is measurable to the limiting nadir precision (1%) in all but the lowest surface reflectance and highest solar zenith angle conditions. In limb measurement, N_2O can be measured to a precision limited only by spacecraft jitter ($\leq 10\%$) up to 30 km, and to about 40% up to 35 km. The total stratospheric N_2O will be precise to 10%; tropospheric columns should be obtainable by subtraction to 5% or better. The temperature dependence of the multiple N_2O lines may provide some information on the vertical distribution of tropospheric N_2O .

2.2 Polluted troposphere molecules

HCHO absorbs between 250 and 360 nm, with its strongest absorption between 300 and 350. The short wavelength absorption is strongly obscured by O_3 absorption, leaving a contribution between about 300 and 350 nm. This window is highly dependent on the O_3 concentration and the viewing geometry and the temperature and concentration of tropospheric O_3 (increased absorption by warm tropospheric ozone will further obscure the HCHO). HCHO is measurable in the nadir view, chiefly at low latitudes. The sensitivity for HCHO measurements with this concentration is 5. Thus, moderately enhanced HCHO can be observed with modest precision and major pollution can be readily measured. Note that this signal to noise ratio is determined using only the portions of the HCHO spectrum close to 350 nm, which remain reasonably unobscured by O_3 . The sensitivity increases by as much as a factor of 2 under conditions of low column O_3 .

SO_2 absorbs between 290 and 315 nm. It is observable in the nadir view, and under conditions of low tropospheric ozone, in the polluted troposphere. For a tropospheric concentration of 20 ppbv (moderate pollution in the boundary layer) SCIAMACHY achieves a signal to noise ratio of 60 (i.e., better than 2% precision), but this is highly variable, depending on the O_3 concentration. SO_2 in normal background

concentrations is not observable.

2.3 Ozone hole molecules

ClO absorbs from 220 to 310 nm. It is strongly masked by ozone absorption. Our sensitivity limit for the nadir view varies from about 10^{13} to 10^{15} cm^{-2} , depending on the ozone concentration. We do not expect to be able to detect ClO under normal conditions. Unusually high ClO concentration coupled with low O_3 concentration (which will improve the detection limit substantially), as found in the Antarctic ozone "hole"¹⁵ will make the ClO column observable. An absorption spectrum of ClO calculated using a representative O_3 hole concentration of 1.5×10^{15} cm^{-2} , compared with a synthesis of the nadir spectrum at an 80° solar zenith angle, under moderate ozone hole conditions, gives a precision for ClO column measurements of 10%.

OCIO absorbs strongly between 280 and 440 nm. It is formed in the atmosphere from the reaction of BrO with ClO and destroyed by photolysis. OCIO has been observed using its structured absorption between 320 and 420 nm at night over Antarctica in spring (column densities of 1×10^{14} molecule cm^{-2}).^{16,17} Using our synthesized nadir spectrum for moderate ozone hole condition and the OCIO absorption for 1×10^{14} cm^{-2} , corresponding to a twilight concentration, we obtain a 2% measurement precision for OCIO. For a typical daytime concentration (2×10^{13} cm^{-2}) we can measure to 10% precision. It may be possible to obtain OCIO profile information at ozone hole concentrations using lunar occultation; insufficient profile modeling is available to accurately estimate the profile limits.

BrO has been measured in the Antarctic spring using its UV absorption.¹⁷ By comparing the absorption of BrO for a nadir concentration of 2.5×10^{13} for our ozone hole geometry, we determine that we can measure this column density of BrO with a precision of 10%. Under normal conditions, the BrO column density is 1.5×10^{13} , implying measurements to 15%. BrO profile ranges are estimated using MPI 2-D models calculations. With solar occultation, BrO in normal concentrations can be measured to 25% from 15-35 km. In limb measurements, BrO profiles can be determined to 50% precision from 20-25 km in normal concentrations and ca. 30% in ozone hole concentrations.

2.4 Surface reflectance and solar zenith angle studies

Absolute radiometric calibration of the SCIAMACHY instrument, combined with direct solar observations, will provide new global information about surface spectral reflectance in the range 300-2400 nm. Although the spatial resolution of SCIAMACHY is limited, this data will be very useful scientifically. Further studies of the retrieval of the reflectance measurements by SCIAMACHY will be made in Phase B.

Surface reflectance and solar zenith angle considerations for molecule measurements in nadir viewing are coupled together since the increased path due to larger solar zenith angle can offset decreased light due to lower reflectance for those molecules measured at wavelengths that penetrate fully to the ground. The increased path can also exacerbate measurements of tropospheric molecules made at shorter wavelengths due to increased loss of tropospheric information because of increased Rayleigh scattering in the stratosphere. Our standard conditions for sensitivity studies (35° N: 63° solar zenith angle; albedo = 0.3) are fairly stringent in the sense that, for the suite of molecular measurements by SCIAMACHY, the deterioration in global coverage due to lower reflectance and other solar zenith angles is not severe. The losses that do occur are mainly in tropospheric measurements.

Surface reflectances and solar zenith angles other than our standard conditions have their greatest impacts on the following measurements: Tropospheric O_3 . At 320 nm, 13% of the light measured by SCIAMACHY at our standard 35° N (63° solar zenith angle) is reflected from the ground. For albedo = 0.1, this decreases to 3.6%, and the precision for tropospheric O_3 is a factor of 2 lower. Losses in tropospheric O_3 information are partly compensated for by increased solar zenith angle, since the light at the red end of the Huggins bands has significant penetration to quite high solar zenith angle. Tropospheric NO_2 is measured at

modest precision in our standard conditions, in a wavelength range where Rayleigh scattering is not a major problem. Sensitivity to tropospheric NO_2 varies roughly as the square root of the reflectance. Measurements of the tropospheric columns of HCHO and SO_2 will suffer with decreased reflectance. HCHO sensitivity will increase almost linearly with the increased path due to higher zenith angle, up to quite high angle, because of the long wavelength extent of the spectrum. SO_2 sensitivity changes with zenith angle will be small. ClO , OCIO , and BrO column measurements were calculated at a high solar zenith angle (80°), appropriate to measurements by *SCIAMACHY* in ozone hole conditions. ClO is measured at such short wavelengths that changes in surface reflectance are not a serious consideration in measurement sensitivity; variability in O_3 has a much more serious impact. ClO will generally be seen at high solar zenith angles, so that sensitivity vs. zenith angle is not an important issue. OCIO is also generally seen at these high zenith angles. Its measurement is more sensitive to surface reflectance since the spectrum extends well beyond 400 nm. Fortunately, the climatology of OCIO is such that measurements will generally occur in regions of high surface reflectance; exceptions occur when the ozone hole conditions extend over ice-free ocean waters. Even in these conditions, the strength of the absorption in the 300-350 nm range ensures useful measurement sensitivity. The spectrum of BrO has its major absorption in the 300-350 nm range, long enough that O_3 absorption is not a serious problem and short enough that lower surface reflectance also will not seriously hamper its measurement. BrO measurement under normal conditions (i.e., away from O_3 -depleted polar regions) will be decrease as the path length decreases due to lower solar zenith angle.

3. AEROSOL STUDIES

The presence of aerosols in climatic models leads to a more important energy deposition in the stratosphere and to a cooling of the troposphere. More recently, the Antarctic ozone hole phenomenon has been explained by the conversion of HCl to ClO by heterogeneous reactions on the surfaces of polar stratospheric clouds.

The *SCIAMACHY* instrument will obtain aerosol data in occultation, limb-scattering and nadir measurements. The high resolution permits distinction between gases and aerosols and will allow altitude distributions and granulometry of the middle-atmospheric aerosols to be obtained. Proper treatment of aerosols in the inversion process also results in more accurate data on the vertical distribution of gases. Simulation and verification of the various types of spectral signatures from different aerosols are an integral part of the *SCIAMACHY* data system development plan.

3.1 Stratospheric Aerosols

Stratospheric aerosols have been extensively studied from balloon and space experiments over the last 30 years: The measurements show spherical particles in the stratosphere composed of a mixture of sulfuric acid and water. These are divided between layers of large particle size, the Junge layer (typical size $0.15 \mu\text{m}$), and a background layer of aerosols of significantly smaller size (ca. $0.05 \mu\text{m}$). However, in the polar stratospheric clouds associated with the Antarctic ozone hole, particle sizes larger than $1 \mu\text{m}$ have been conjectured. Other types of suspended particles exist in the upper atmosphere, from meteoric decay; little is known about them except that their metallic cores give them an important imaginary refractive index and that the resulting increase of Mie scattering efficiencies makes them more observable, as published in visual space observations and balloon data reports. *SCIAMACHY*, through measurements of these latter particles, may help solve the present controversy concerning the geophysical impacts of small meteorites and comets.

3.2 Tropospheric Aerosols

The high spectral resolution of the SCIAMACHY instrument combined with its spatial resolution can lead to study of image contrast, and to a characterization of the nature of tropospheric haze in terms of natural phenomena. For example, sand winds have never been monitored on a global scale. Since they occur by definition mostly in dry regions, the absence of clouds will make SCIAMACHY a perfect sensor for them. SCIAMACHY will also measure the high quantities of soot from forest fires to which, for decades, the blue moon phenomenon has been attributed. Identification of these "clouds" and their continuous observation will lead to an assessment of the effects of these largely local phenomena on the global atmospheric system.

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Table 1

Quantities Retrieved from SCIAMACHY Nadir/Limb Observations

Species	Retrievable Quantity*	Wavelength (nm)	Notes/Applications
O ₃	Profile (S, T)	255-350, 480-680	
O ₂	Profile (S, T)	690, 760	Cloud tops/ boundary layer
O ₂ (¹ Δ)	Profile (S)	1260-1275	Mesospheric O ₃
O ₄	Column (T)	475, 530, 560, 630	Cloud tops/ boundary layer
H ₂ O	Profile (S, T)	700-1000, 2250-2390	
CO	Profile (S), Column (T)	2300-2390	Limited tropospheric profile information
CO ₂	Profile (S, T)	1980-2020	P, T retrievals
CH ₄	Profile (S, T)	2250-2390	
HCHO	Column (T) [†]	310-360	Biomass burning, tropical vegetation
SO ₂	Column (T) [†]	290-310	Industrial pollution, volcanos
NO	Profile (S)	255-280	Above 40 km in emission
NO ₂	Profile (S), Column (T) [†]	300-600	Lightning, combustion
NO ₃	Profile (S)	660-665	Lunar occultation
N ₂ O	Profile (S), Column (T)	2250-2300	Limited tropospheric profile information
ClO	Column (S) [‡]	300-310	Polar regions in spring
OCIO	Column (S) [‡]	320-420	Polar regions in spring
BrO	Profile (S)	310-345	

* S = stratosphere; T = troposphere. Mesosphere not included in this table.

[†]Observable in regions with relatively high concentrations.

[‡]Observable in perturbed "O₃ hole" regions.